



6.6 CHEMICAL COMPOSITION OF PARTICULATE MATTER AEROSOLS AT URBAN AND NONURBAN SITES

This section summarizes selected data from a number of studies for the composition of atmospheric particles in suburban, urban, and a few rural areas for comparison purposes. Emphasis has been placed on the Harvard six-city study and the inhalable particulate network (1980-1981). Data for fine particle mass and elemental composition were available from these studies. Data for sulfate, nitrate, and elemental and organic carbon content are included from other studies to provide an overview of the chemical composition of the atmospheric aerosol in the United States. Tables presented in Appendix 6A provide relatively detailed representations of the properties of atmospheric particles to which U.S. populations are exposed. Unfortunately, data this complete are generally collected only during intensive studies. The tables are meant to provide examples of the types of information that could be collected as part of future monitoring efforts in support of human exposure investigations.

A summary of all the aerosol sampling studies included in this compilation is given in Tables 6A-1a, 6A-1b, and 6A-1c. Sampling studies have been grouped by geographical region roughly corresponding to the eastern, central, and western United States. Data are tabulated for the $PM_{2.5}$ ($d < 2.5 \mu m$), the coarse fraction of PM_{10} ($2.5 \mu m < d < 10 \mu m$) and PM_{10} ($d < 10 \mu m$) size fractions of the ambient aerosol in Tables 6A-2a, 6A-2b, and 6A-2c. Compositional data for all size fractions were broken down into the following major components: sulfate, as SO_4^{2-} ; carbon, as organic carbon (OC), which has been multiplied by a factor of 1.4 to account for the presence of oxidized species, and elemental carbon (EC); nitrate as NO_3^- ; and remaining trace elements. The NH_4^+ , that would be required to neutralize all acidic species in the samples, is shown as $(NH_4^+)^*$. Representing sulfate as ammonium sulfate and using a factor of 1.4 to account for the mass of organic carbon present in oxidized forms allows a firm lower limit to be placed on the fractional mass that is not chemically identified in filter samples. Acidity is given in units of $nmoles/M^3$ in Tables 6A-2a and 6A-2c. The masses of the trace elements from sodium through lead have been calculated by assuming they are in their most stable forms for conditions at the earth's surface. Reconstructed masses calculated in this way are shown by the entry, Sum, along with measured masses, and the ratio of the two are shown at the bottom of the individual summaries for each size fraction. Not all compositional categories were measured in the studies for inclusion in the tables. For instance, data for characterizing the carbon or nitrate

content of the ambient aerosol are not available for many of the studies listed. Average data are shown in graphical form in Figures 6-85a, 6-85b, and 6-85c for studies in the eastern, central, and western United States.

As can be seen from inspection of Figure 6-85a, sulfate is the major identified component of mass for fine particles (34.1%), followed by elemental and organic carbon (24.8%), minerals (4.3%), and nitrate (1.1%) for studies in the eastern United States. However, this last inference is based on only a few studies in which nitrate was measured. Pierson et al. (1980a,b, 1989) measured nitrate as constituting only 0.8% to 1.4% of aerosol mass at Allegheny Mountain and Laurel Hill in southwest Pennsylvania in the summers of 1977 and 1983. Presumably, the low nitrate in these and other studies in the eastern United States is related to aerosol acidity. Coarse particles are seen to consist mainly of mineral forming elements (51.8%) and sulfate (4.9%). Not enough data were available to determine abundances of carbon species and nitrate in the coarse fraction. A sizable fraction of both the fine (22.8%) and coarse (41.5%) particle mass is shown as unknown. This unknown mass is assumed to be mainly water, either bound as water of hydration or associated with hygroscopic particles. A small fraction of the mass, especially in the coarse fraction, may be present as carbonates. Carbonates are difficult to quantify, in part because of artifact forming reactions with atmospheric CO₂ and acids on filters. Stable carbonates could be identified by SEM in regions where they are known to represent a substantial fraction of soil composition.

Fine particles sampled in the studies shown in Table 6A-1 in the central United States (Figure 6-85b) are seen to consist mainly of sulfate (22.3%), minerals (7.6%), and elemental and organic carbon (53.6%). The reconstructed mass percentages sum to 124.8%. This could be due to an overestimation of the carbon content which was estimated from only a few samples collected during winter in woodsmoke impacted areas. Coarse particles were found to consist mainly of minerals (62.8%), sulfate (3.1%) and an unknown fraction (33.0%). No nitrate or carbon data were available for the coarse fraction from the studies in the central United States.

While gross fine particle composition appears to be broadly similar between the eastern and central United States on the basis of the studies shown in Tables 6A-1a, 6A-1b, and 6A-1c, the fine particle composition is seen to be distinctly different in the western United States

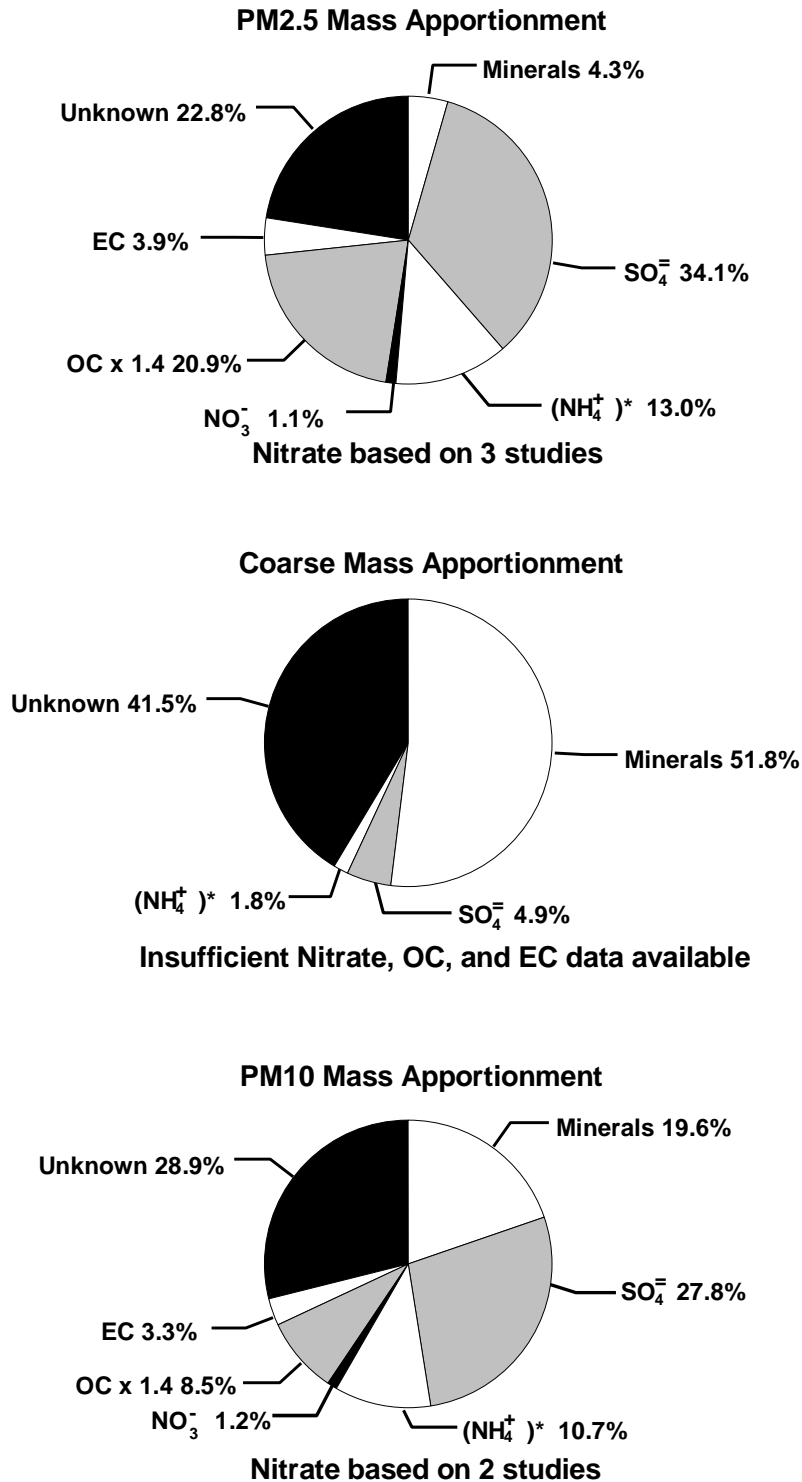


Figure 6-85a. Major constituents of particles measured at sites in the eastern United States, as shown in Tables 6A-2a, 6A-2b, and 6A-2c. (NH₄⁺)^{*} represents the concentration of NH₄⁺ that would be required if all SO₄²⁻ were present as (NH₄)₂SO₄ and all NO₃⁻ as NH₄NO₃. Therefore, (NH₄⁺)^{*} represents an upper limit to the true concentration of NH₄⁺.

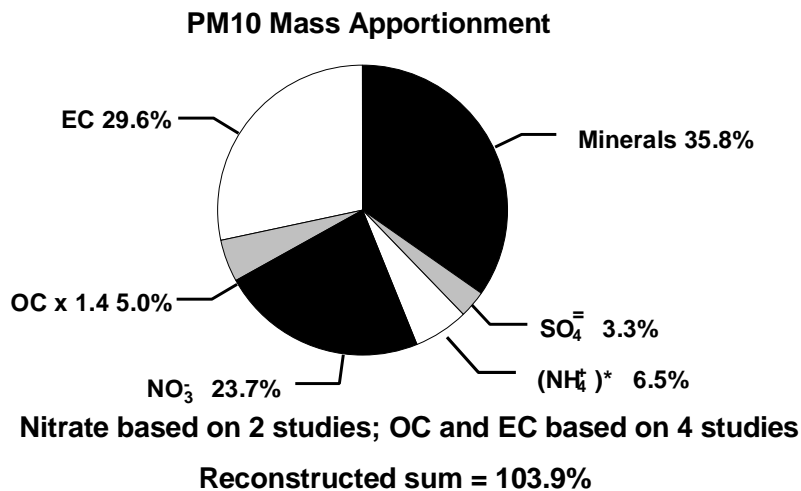
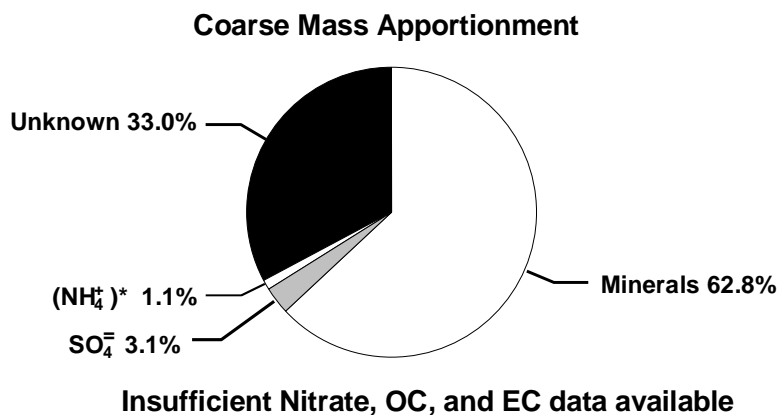
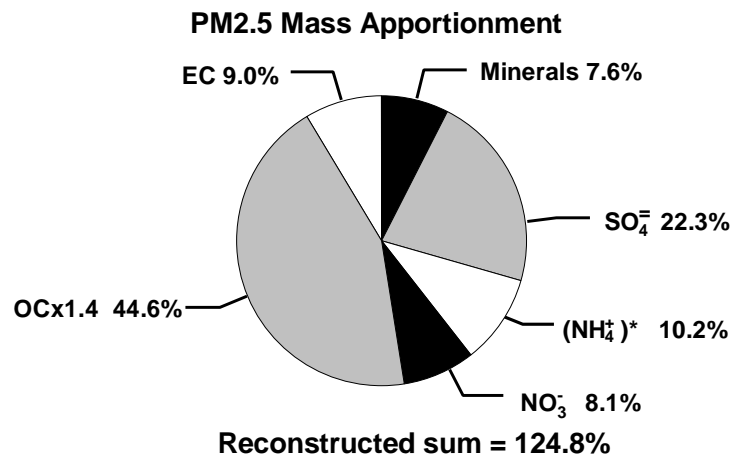


Figure 6-85b. Major constituents of particles measured at sites in the central United States, as shown in Tables 6A-2a, 6A-2b, and 6A-2c. (NH₄⁺)^{*} represents the concentration of NH₄⁺ that would be required if all SO₄ were present as (NH₄)₂SO₄ and all NO₃⁻ as NH₄NO₃. Therefore, (NH₄⁺)^{*} represents an upper limit to the true concentration of NH₄⁺.

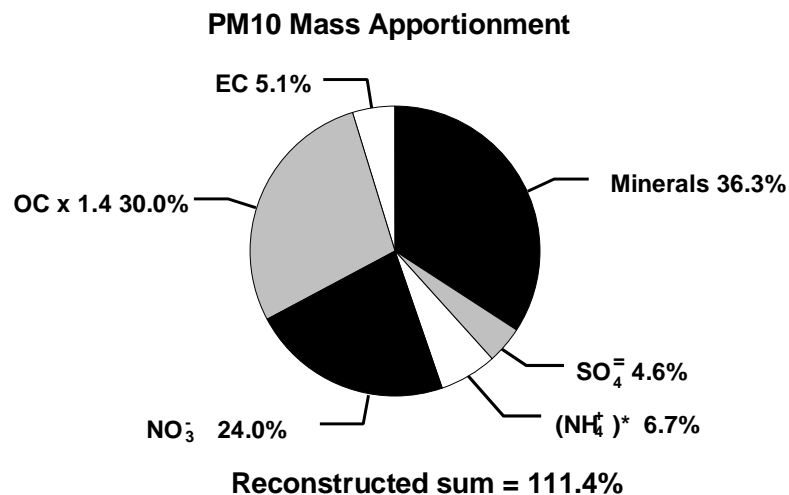
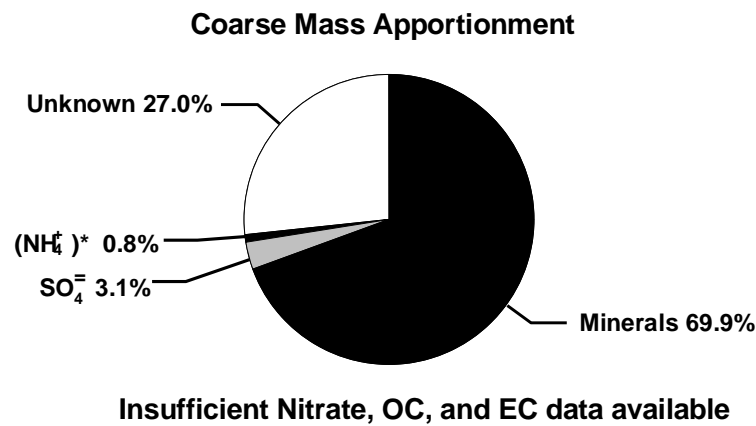
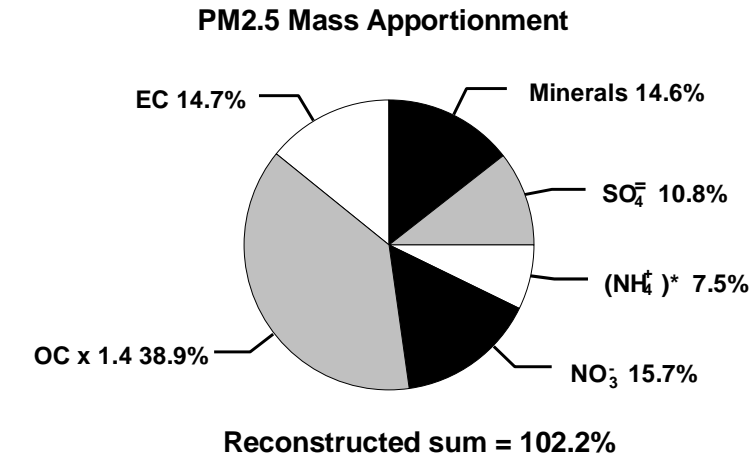


Figure 6-85c. Major constituents of particles measured at sites in the western United States, as shown in Tables 6A-2a, 6A-2b, and 6A-2c. (NH₄⁺)^{*} represents the concentration of NH₄⁺ that would be required if all SO₂ were present as (NH₄)₂SO₄ and all NO₃⁻ as NH₄NO₃. Therefore, (NH₄⁺)^{*} represents an upper limit to the true concentration of NH₄⁺.

(Figure 6-85c). Elemental plus organic carbon species (53.6%) are the major identified component of mass, instead of sulfate (10.8%), and minerals and nitrate account for a larger fraction of total mass. While minerals are seen to account for most of the coarse particle mass (69.9%), available data were insufficient to estimate the contributions of elemental and organic carbon species to the coarse mass. Table 6A-3 shows a comparison of selected ratios of mass components for studies conducted in each of the three broad regions of the United States.

Many of the studies listed in Table 6A-3 involved data collected at more than one site within an airshed. Information about the variability of particle mass within an airshed can yield information about the nature of sources of the particles. The variability of mean concentrations measured at multiple sites within a study area is used as a measure of the intersite variability in fine particle composition and is shown in Tables 6A-4a and 6A-4b.

6.7 ACID AEROSOLS

6.7.1 Introduction

Acid aerosols are secondary pollutants formed primarily through oxidation of sulfur dioxide (SO_2), a gas emitted by the combustion of fossil fuels. Oxidation of SO_2 forms sulfate (SO_4^-), the major component of acid aerosols. Sulfate is formed to a lesser extent through the oxidation of sulfur species (H_2S and CH_3SCH_3) from natural sources. The oxidation of SO_2 occurs through a series of heterogeneous (gas-particle) or homogeneous (gas or aqueous) phase oxidation reactions that convert SO_2 to sulfuric acid (H_2SO_4) particles. The sulfate species are typically expressed in terms of total SO_4^- , with the acidic fraction expressed in terms of titratable H^+ ($[\text{H}^+] + [\text{HSO}_4^-]$) and referred to as aerosol strong acidity. The chemical aspects of oxidation of SO_2 and formation of aerosol strong acidity are discussed in Chapter 3, Section 3.3.1. H^+ is usually found in the fine particle size fraction (aerodynamic diameter (D_p) $< 1.0 \mu\text{m}$) (Koutrakis and Kelly, 1993; Pierson et al., 1980a, 1989). However, acidity may be found in larger particles during periods of fog or very high relative humidity. Keeler et al. (1988) and Pierson et al. (1989) report finding acidity in the $> 2.5 \mu\text{m}$ size range when the relative humidity was close to 100%. Although recent research has shown a high correlation between SO_4^- and acidity, data from summertime sampling have shown that SO_4^- is not always a reliable predictor of H^+ for individual events at a given site (Lipfert and Wyzga, 1993).

A major determinant of the lifetime of H^+ in the atmosphere is the rate of neutralization by ammonia (NH_3). Ammonia reacts with H_2SO_4 to form ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ and ammonium bisulfate (NH_4HSO_4). The major sources of ammonia in the environment are animals and humans (Fekete and Gyenes, 1993). The then current state-of-knowledge regarding acid aerosols was reviewed by EPA in 1989 (U.S. Environmental Protection Agency, 1989) and by Spengler et al., 1990. A more recent summary is given by Waldman et al. (1995).

6.7.2 Geographical Distribution

In North America, ambient concentrations of H^+ tend to be regional in nature with the highest concentrations found in the northeastern United States and southwestern Canada. Spengler et al. (1990) have collected information on maximum values of SO_4^- and H^+ found across the U.S. and southern Canada. This information is shown in Table 6-5.

6.7.3 Spatial Variation (Regional-Scale)

Recent evidence has shown that meteorology and regional transport are extremely important to acid sulfate concentrations. Elevated levels of ambient H^+ were measured simultaneously during a regional episode at multiple sites located from Tennessee to Connecticut (Keeler et al., 1991). Lamborg et al. (1992) measured H^+ concentrations to investigate the behavior of regional and urban plumes advecting across Lake Michigan. Results suggested that aerosol acidity is maintained over long distances (up to 100 km or more) in air masses moving over large bodies of water. Lee et al. (1993) reported that H^+ and SO_4^- concentrations measured in Chicago over a year were similar to levels measured in St. Louis. In an analysis of acid sulfate concentrations measured at Pittsburgh, State College, and Uniontown, PA, Liu et al. (1996) reported high correlations for H^+ between all three locations. The three locations are separated by large distances (approximately 60 to 240 km) and have vastly different population densities. It is commonly believed that the source region for most of the H^+ precursors (primary inorganic pollutant gases — SO_2 and NO_x) is the Ohio River Valley (Liroy et al., 1980). The conversion of the primary gases to secondary pollutants takes place as the prevailing winds carry the precursors

**TABLE 6-5. MAXIMUM SO_4^- AND H^+ CONCENTRATIONS
MEASURED AT NORTH AMERICAN SITES
(H^+ concentrations expressed as sulfuric acid (H_2SO_4) equivalents;
"SC" indicates semi-continuous measurements.)**

Location	Sample Duration (h)	Maximum Concentration	
		$\text{SO}_4^- (\mu\text{g}\cdot\text{m}^{-3})$	$\text{H}_2\text{SO}_4 (\mu\text{g}\cdot\text{m}^{-3})$
Lennox, CA	2-8	18	0.1
Smoky Mountains	12	17	10
High Point, NJ	6	37	18
Brookhaven, NY	3	24	10
Tuxedo, NY	1-12	41	9
St. Louis, MO	SC	25	7
St. Louis, MO	SC	43	34
Los Angeles, CA	12	10	3
Harriman, TN	SC	47	18
Watertown, MA	SC	31	14
Fairview Lake, NJ	SC,4	27	12
Warren, MI	24	37	9
Whiteface Mt., NY	24	59	14
Toronto, ON, Canada	8,16	75	19
Allegheny Mt., PA	7,10	45	31
Laurel Hill, PA	7,10	56	42
Harriman, TN	24	28	14
St. Louis, MO	24	40	6
Topeka, KS	24	14	3
Watertown, MA	24	23	9
Steubenville, OH	24	56	18
Portage, WI	24	33	4
Kanawha Valley, WV	24	46	22
Dunville, ON, Canada	24	31	15
Hendersonville, TN	24	23	11
Livermore, CA	24	9	2
Morehead, KY	24	23	14
Monroeville, PA	24	42	18
Pembroke, ON, Canada	24	29	14
Springdale, AR	24	11	2
Newtown, CT	24	26	8
Allegheny Mt., PA	12	33	20
Uniontown, PA	12,24	52	39
State College, PA	12	47	25
Philadelphia, PA	24	39	9
Pittsburgh, PA	6,24	27	15

Source: Spengler et al. (1990).

from the source region, northeastward to the northeastern United States and southwestern Canada. This type of northeasterly wind flow occurs on the backside (western side) of mid-latitude anti-cyclones (high pressure systems).

Pierson et al. (1980a,b, 1989) conducted studies of atmospheric acidity on Allegheny Mountain and Laurel Hill in southwest Pennsylvania, 80 and 100 km southeast of Pittsburgh, in the summers of 1977 and 1983. The aerosol H^+ appeared to represent the net after H_2SO_4 reaction with $\text{NH}_3(\text{g})$. The resulting H^+/SO_4^- ratio depended on SO_4^- concentration, approaching that of H_2SO_4 at the highest SO_4^- concentrations. The atmosphere was acidic; the average concentrations of HNO_3 (78 nmole/ m_3) and aerosol H^+ (205 nmole/ m_3), NH_4^+ (172 nmole/ m_3), and SO_4^- (201 nmole/ m_3), and the dearth of NH_3 (<15 nmole/ m_3), show that the proton acidity of the air exceeded the acid-neutralizing capacity of air by a factor of >2, with one 10-hour period averaging 263 nmole/ m_3 for HNO_3 and 844 nmole/ m_3 for H^+ . SO_2 added another 900 nmole/ m_3 (average) of potential H^+ acidity. HNO_3 and aerosol H^+ episodes were concurrent, on 7-8 day cycles, unrelated to SO_2 which existed more in short-lived bursts of apparently more local origin. NO_x was sporadic like SO_2 . Laurel and Allegheny, separated by 35.5 km, were essentially identical in aerosol SO_4^- , and in aerosol H^+ , less so in HNO_3 ; apparently, chemistry involving HNO_3 and aerosol H^+ or SO_4^- was slow compared to inter-site transport times (1-2 hours). From growth of b_{scat} and decline of SO_2 , daytime rate coefficients for SO_2 oxidation and SO_2 dry deposition were inferred to have been, respectively, ~ 0.05 and $\leq 0.1 \text{ hr}^{-1}$.

HNO_3 declined at night. Aerosol H^+ and SO_4^- showed no significant diurnal variation, and O_3 showed very little; these observations, together with high PAN/ NO_x ratios, indicate that regional transport rather than local chemistry is governing. The O_3 concentration (average 56 ppb or 2178 nmole/ m_3) connotes an oxidizing atmosphere conducive to acid formation.

Highest atmospheric acidity was associated with (1) slow westerly winds traversing westward SO_2 source areas, (2) local stagnation, or (3) regional transport around to the back side of a high pressure system. Low acidity was associated with fast-moving air masses and with winds from the northerly directions; upwind precipitation also played a moderating role in air parcel acidity. Much of the SO_2 and NO_x , and ultimately of the HNO_3 and aerosol H^+ , appeared to originate from coal-fired power plants. An automotive contribution to the NO_x and HNO_3 could not be discerned.

Size distributions of aerosol H^+ and SO_4^- were alike, with MMED $\sim 0.7 \mu\text{m}$, in the optimum range for efficient light scattering and inefficient wet/dry removal. Thus, light scattering and visual range degradation were attributable to the acidic SO_4^- aerosol. With inefficient removal of aerosol H^+ , and inefficient nighttime removal of HNO_3 , strong acids may be capable of long-distance transport in the lower troposphere. Water associated with the acidic aerosol was shown to account for much of the light scattering.

6.7.4 Spatial Variation (City-Scale)

A study of acid aerosols and ammonia (Suh et al., 1992) found no significant spatial variation of H^+ at Uniontown, Pennsylvania, a suburb of Pittsburgh. Measurements at the central monitoring site accounted for 92% of the variability in outdoor concentrations measured at various homes throughout the town. There was no statistical difference ($p > 0.01$) between concentrations of outdoor H^+ among five sites (a central site and four satellite sites) in Newtown, Connecticut (Thompson et al., 1991). However, there were differences in peak values which were probably related to the proximity of the sampling sites to ammonia sources. These studies suggest that long-term averages should not substantially differ across a suburban community, although peak values may differ significantly.

In small suburban communities outdoor concentrations of H^+ are fairly uniform, suggesting that minor differences in population density do not significantly affect outdoor H^+ or NH_3 concentrations (Suh et al., 1992). In urban areas, however both H^+ and NH_3 exhibit significant spatial variation. Waldman et al. (1990) measured ambient concentrations of H^+ , NH_3 , and SO_4^- at three locations in metropolitan Toronto. The sites, located up to 33 km apart, had significant differences in outdoor concentrations of H^+ . Waldman and co-workers reported that the sites with high NH_3 measured low H^+ concentrations. However, the limited number of sampling sites did not allow for a conclusive determination of the relationship between population density, ammonia concentrations, and concentrations of acid aerosols.

An intensive monitoring study has been conducted during the summers of 1992 and 1993 in Philadelphia (Suh et al., 1995). Twenty-four hour measurements of aerosol acidity (H^+) sulfate and NH_3 were collected simultaneously at 7 sites in metropolitan Philadelphia and at Valley Forge, 30 km northeast of the city center. The researchers reported that SO_4^- was evenly

distributed throughout the measurement area but H^+ concentrations varied spatially within metropolitan Philadelphia. This variation was related to local NH_3 concentrations and the local population density (Figure 6-86). The amount of NH_3 available to neutralize H^+ increased with population density, resulting in lower H^+ concentrations in more densely populated areas. The extent of the spatial variation in H^+ concentrations did not appear to depend on the overall H^+ concentration. It did, however, show a strong inverse association with local NH_3 concentrations.

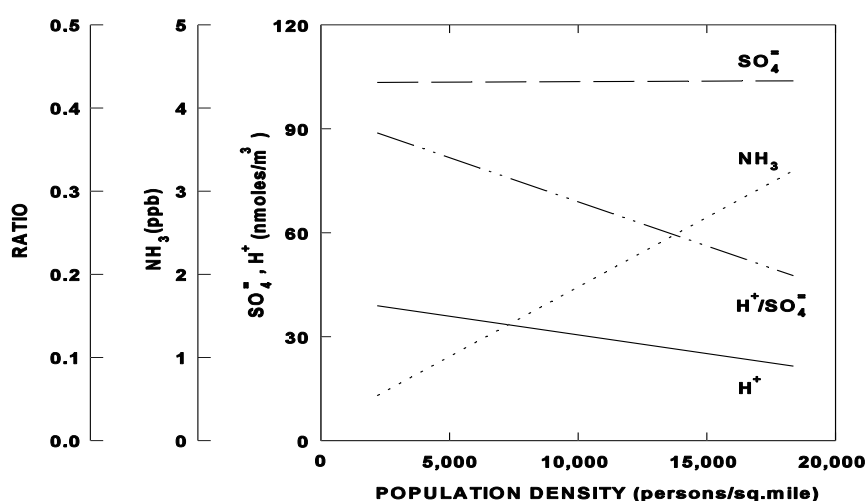


Figure 6-86. Mean air pollutant concentrations for days when winds were from the southerly direction, plotted versus population density. The solid line represents H^+ concentrations; the long dashed line represents SO_4^{2-} concentrations; the dashed and dotted line represents the ratio of H^+ to SO_4^{2-} levels; and the dotted line represents NH_3 concentrations. All data collected in Philadelphia, PA, during the summers of 1992 and 1993.

Source: Adapted from Suh et al. (1995).

6.7.5 Seasonal Variation

An analysis of results from Harvard's 24-City Study (Thompson et al., 1991), which measured acid aerosols concentrations at 8 different small cities across North America each year during a three year period, revealed that the summer H^+ mean concentrations were significantly higher than the annual means at all sites. The results showed that at the sites with high H^+ concentrations, approximately two-thirds of the aerosol acidity occurred from May through

September (Figure 6-87). Little or no seasonal variation was observed at sites with low acidity. These findings were supported by those of Thurston et al. (1992) in which H^+ concentrations measured at Buffalo, Albany, and White Plains, NY, were found to be highest during the summertime. Thurston and co-workers also reported that moderate concentrations of H^+ could occur during non-summer months

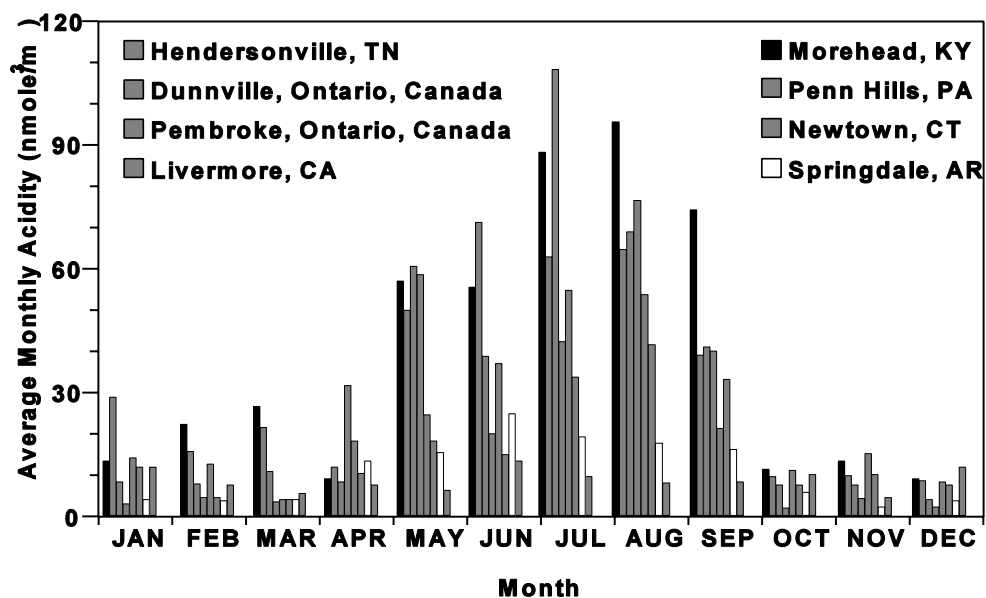


Figure 6-87. Average monthly aerosol strong acidity for Year 1 sites of the Harvard 24-City Study.

Source: Thompson et al. (1991).

6.7.6 Diurnal Variation

Evidence exists of a distinct diurnal pattern in outdoor H^+ concentrations. Wilson et al. (1991) examined concentration data for H^+ , NH_3 , and SO_4^- from the Harvard 24-City Study for evidence of diurnal variability (Figure 6-88). This investigation found a distinct diurnal pattern for H^+ concentrations and the H^+/SO_4^- ratio, with daytime concentrations being substantially

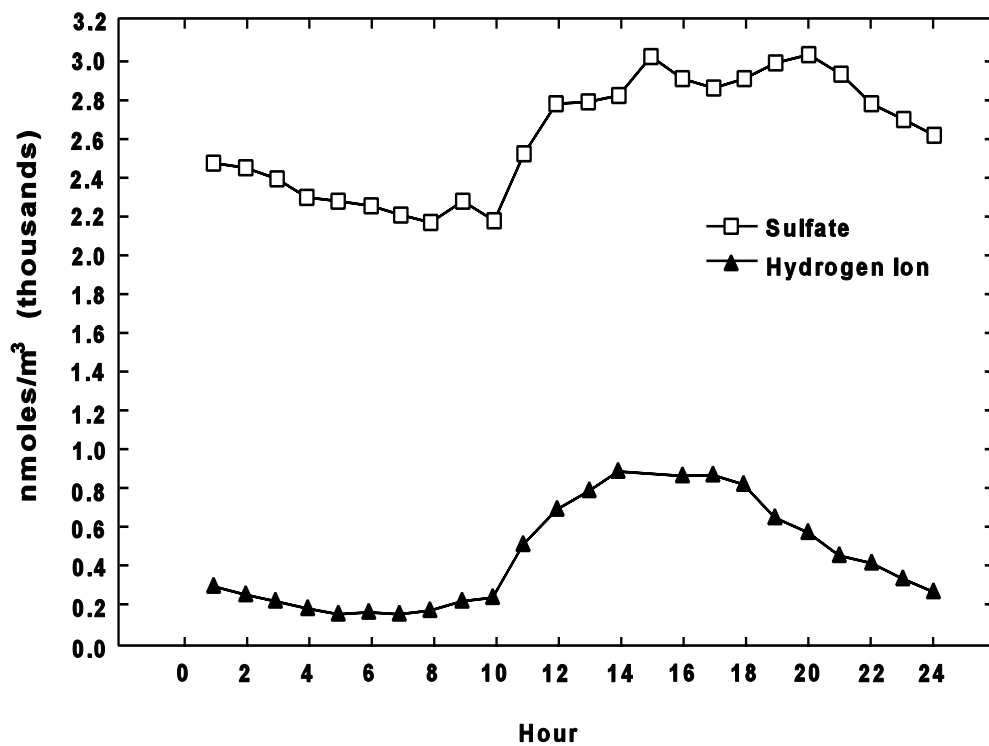
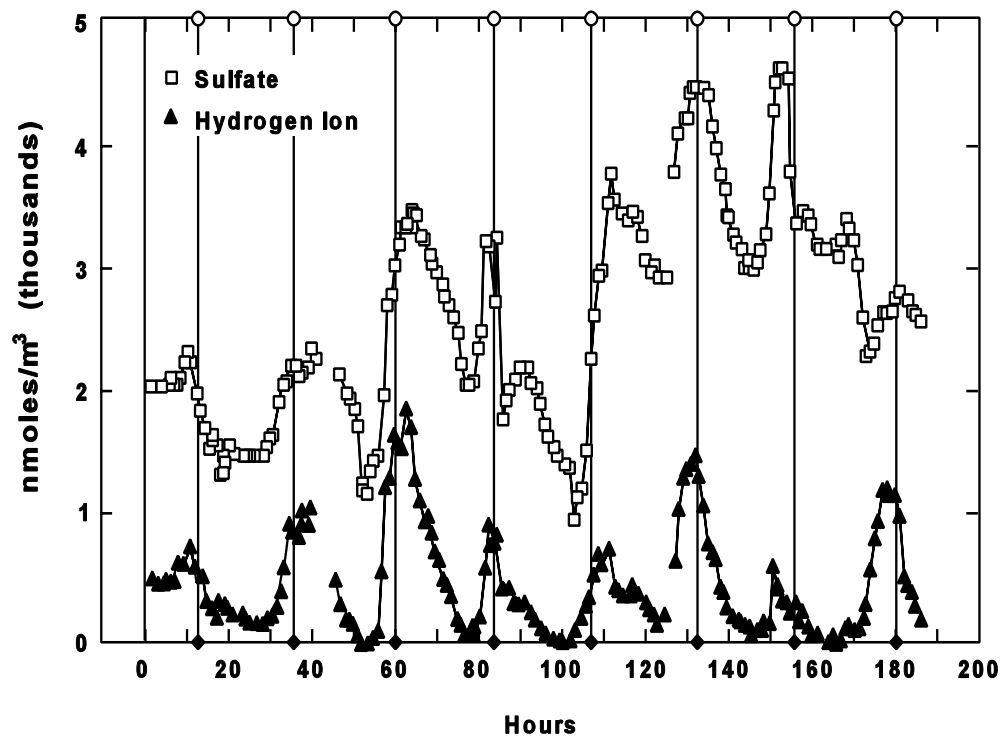


Figure 6-88. Diurnal pattern of sulfate and hydrogen ion at Harriman, TN, weekly pattern and daily average.

Source: Wilson et al. (1991).

higher than nighttime levels. Both H^+ and SO_4^- concentrations peaked between noon and 6:00 pm. No such diurnal variation was found for NH_3 . Wilson and co-workers concluded that the diurnal variation in H^+ and SO_4^- was probably due to atmospheric mixing. Air containing high concentrations of H^+ and SO_4^- mixes downward during daylight hours when the atmosphere is unstable and well-mixed. During the night, ammonia emitted from ground-based sources neutralizes the acid in nocturnal boundary layer, the very stable lower part of the atmosphere, but a nocturnal inversion prevents the ammonia from reacting with the acid aerosols aloft. Then in the morning as the nocturnal inversion dissipates, the acid aerosols mix downward again as the process begins anew. Spengler et al. (1986a) also noted diurnal variations in sulfate and sulfuric acid concentrations and suggested atmospheric dynamics as the cause. The diurnal variation in SO_4^- has been observed by other workers and discussed in terms of atmospheric dynamics by Wolff et al. (1979) and Wilson and Stockberger (1990).

This diurnal variation in mixing heights and concentrations does not seem to hold at elevated sites. For example, Pierson et al. (1980a,b, 1989) found no appreciable night/day difference in aerosol H^+ (or NH_4^+ or SO_4^-), and almost no diurnal variation in O_3 , at two elevated sites (Allegheny Mountain and Laurel Hill, elevations 838 and 850 m) in southwest Pennsylvania. They contrasted this behavior with that at lower sites, and particularly with the concurrent measurements at Deep Creek Lake (Vossler et al., 1989). The differences were attributed to isolation from ground-based processes at the elevated sites at night.

6.7.7 Indoor and Personal Concentrations

Several studies have examined indoor concentrations of acid aerosols and personal monitoring. Brauer et al. (1989) monitored personal exposures to particles (including acidic sulfates) and gases in metropolitan Boston in the summer of 1988, and compared these to measurements collected at a centrally located ambient monitor. They found that personal concentrations of acidic aerosols and gases differed significantly from those measured at the centrally located site. Summer and winter concentrations of acid aerosols and gaseous pollutants also collected in Boston (Brauer et al., 1991) showed indoor/outdoor ratios of H^+ to be 40-50% of the indoor/outdoor SO_4^- ratio indicating neutralization of the acid by the higher indoor NH_3 levels, which were reported.

Indoor, outdoor, and personal acid aerosol monitoring was performed for children living in Uniontown, Pennsylvania, during the summer of 1990 (Suh et al., 1992). The indoor, outdoor, and personal measurements were compared to outdoor measurements collected from a centrally located ambient monitor. Personal concentrations were lower than corresponding outdoor levels but higher than indoor levels. Air conditioning was found to be an important predictor of indoor H^+ , while NH_3 was found to influence indoor and personal H^+ concentrations. Similar results were obtained in a study of the relationships between indoor/outdoor concentrations of H^+ and NH_3 conducted in State College, PA, in 1991 (Suh et al., 1994).

In a study characterizing H^+ concentrations at child and elderly care facilities, Liang and Waldman (1992) measured indoor and outdoor acid aerosol concentrations. Results from this study showed that indoor/outdoor H^+ and SO_4^- ratios were comparable to those measured inside residential buildings. Air conditioner use and indoor NH_3 concentrations were again identified as important determinants of indoor H^+ concentrations.

6.8 NUMBER CONCENTRATION OF ULTRAFINE PARTICLES

6.8.1 Introduction

Recent work has suggested that ultrafine particles may be responsible for some of the health effects associated with exposure to particulate matter (Chapter 11, Section 11.4). The hypothesis for explaining a biological effect of ultrafine particles is based on the number, composition and size of particles rather than their mass (Seaton et al., 1995). This has led to an interest in the number concentration of ambient particles. This section examines data on particle number concentration and the relationship between particle number and particle mass or volume.

6.8.2 Ultrafine Particle Number-Size Distribution

In the context of ambient particles, the term ultrafine particles refers to those particles with diameters below $0.1\ \mu\text{m}$. Ultrafine aerosol size distributions from an urban site at Long Beach, California (Karch et al., 1987), and from a background site in the Rocky Mountains, Colorado (Kreidenwies and Brechtel, 1995) are shown in Figures 6-89 and 6-90. Both of these sets of data were obtained by electrical mobility measurements. For the urban aerosols of Long Beach, the

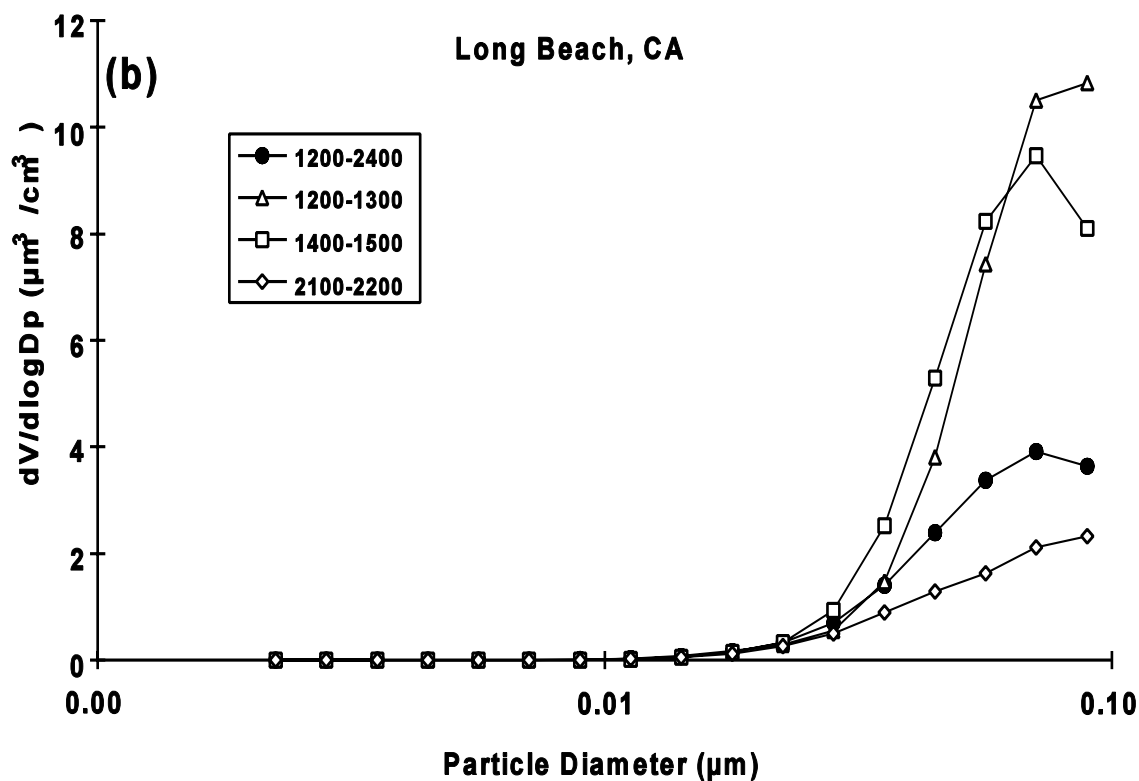
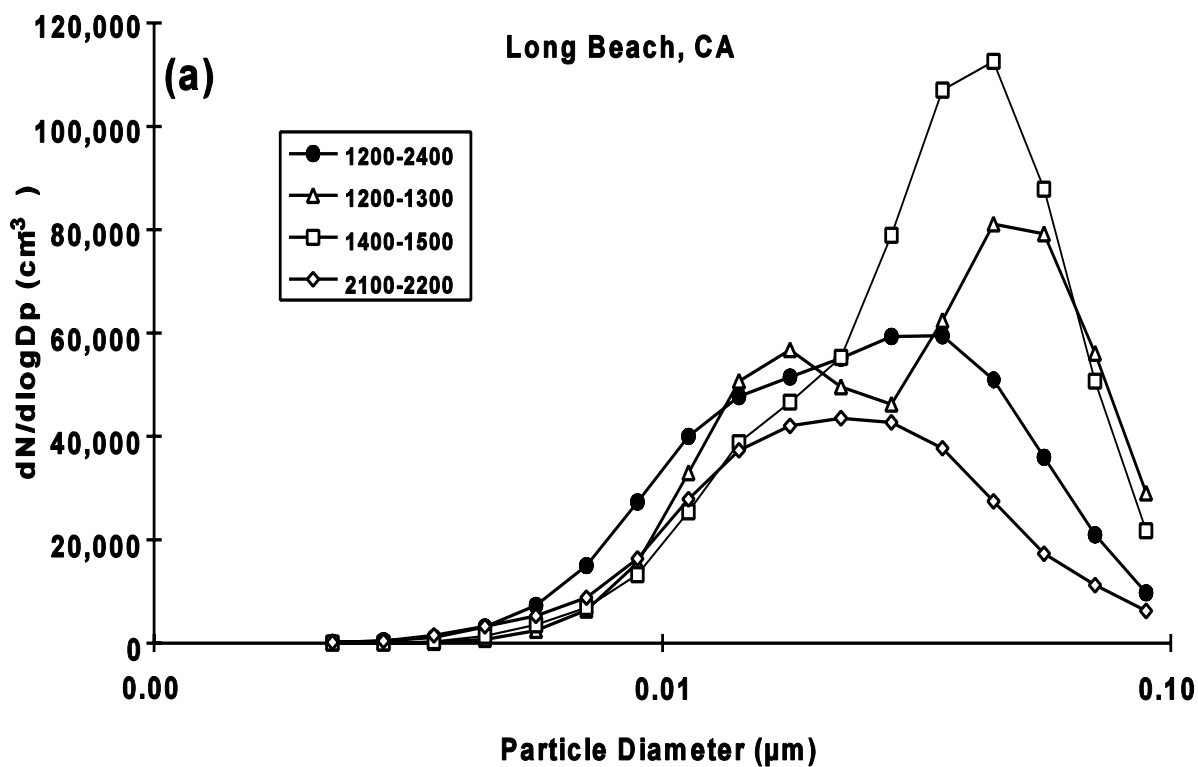


Figure 6-89. Aerosol number (a) and volume (b) size distributions from an urban site at Long Beach, CA.

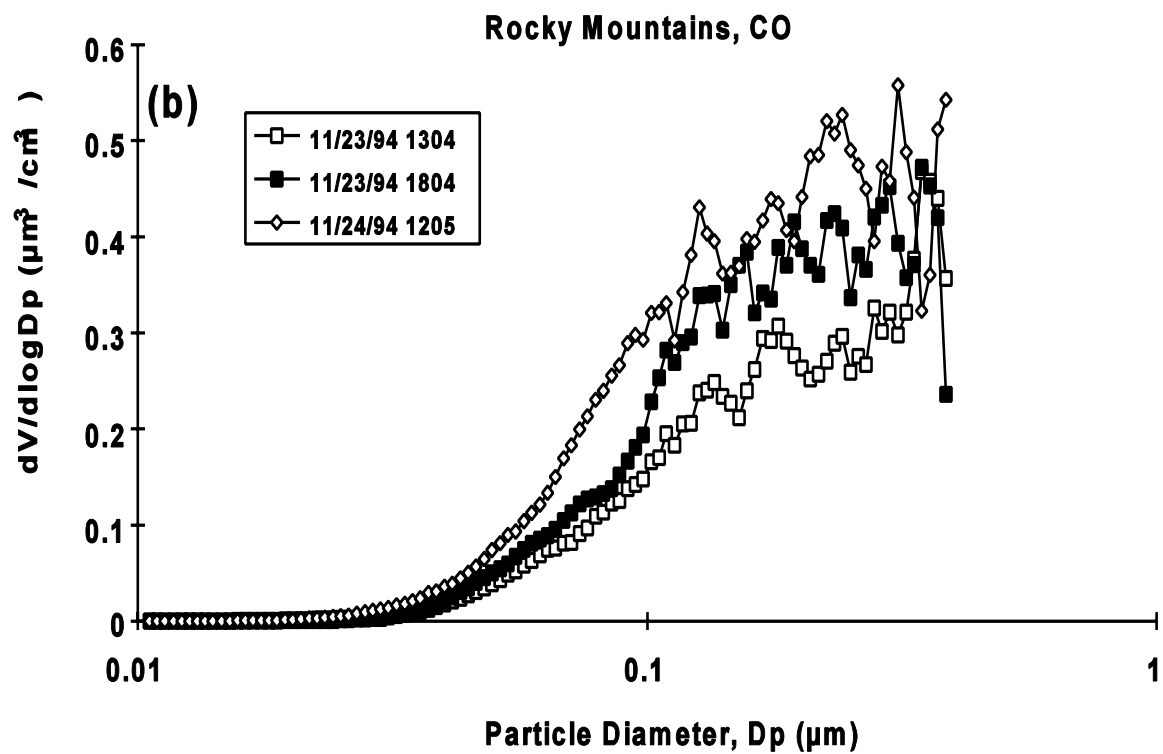
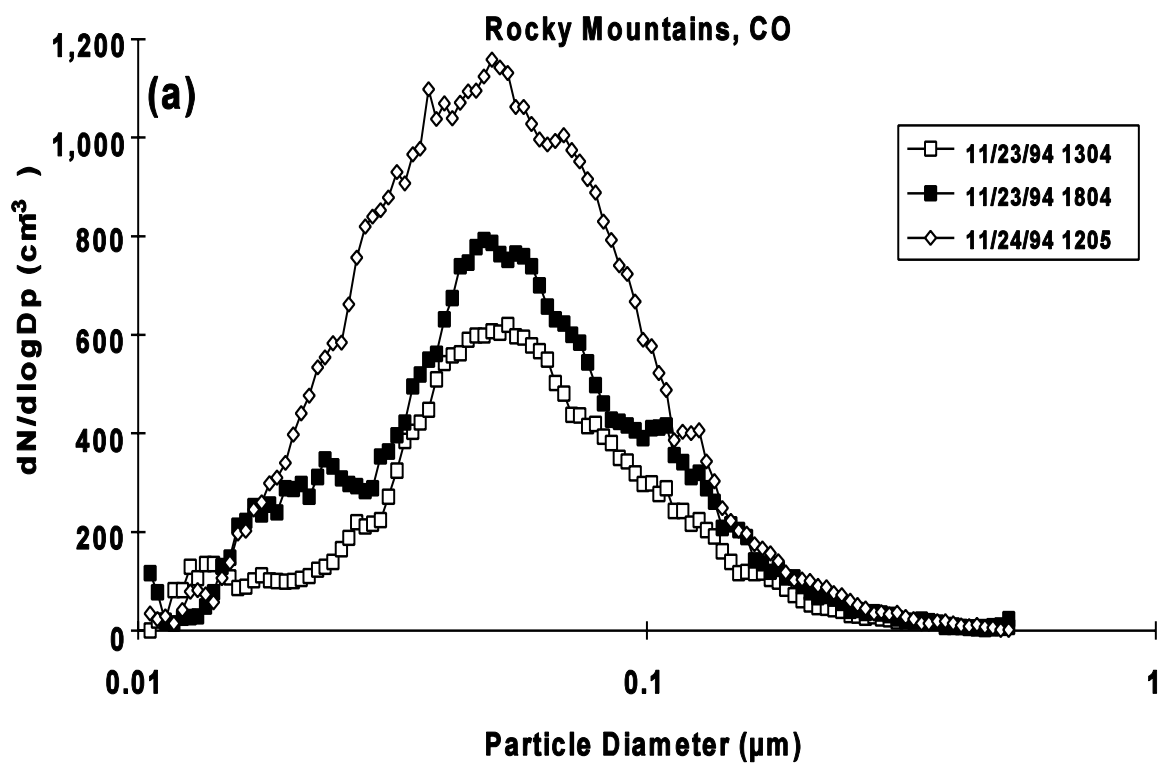


Figure 6-90. Aerosol number (a) and volume (b) size distributions from a background site in the Rocky Mountains, CO.

number geometric mean diameter can vary from $0.012\ \mu\text{m}$ to $0.043\ \mu\text{m}$. Some of the ultrafine distributions, such as that shown for the 1,200 to 1,300 PST time period, are bimodal. The number concentrations were higher in the early afternoon, 1400-1500 PST, as shown in Figure 6-91. For the background aerosols from Rocky Mountains the number geometric mean diameter of the ultrafine aerosols was somewhat larger than for Long Beach, with geometric mean diameters ranging from 0.047 to $0.075\ \mu\text{m}$ for periods without urban influence. A bimodal character for the ultrafine distribution was also observed for some measurements, as seen in Figure 6-90.

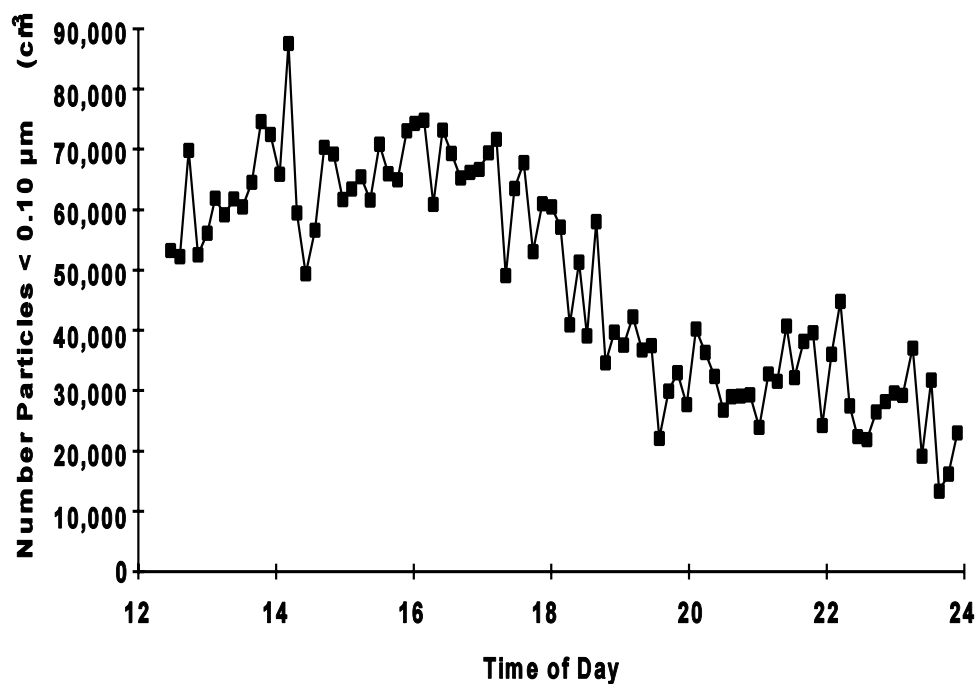


Figure 6-91. Number concentrations as a function of time of day at Long Beach, CA.

The contrast between urban and background ultrafine aerosol size distribution is demonstrated in Figure 6-92, where a change in the wind direction brought transport from an urban area to the background site at Rocky Mountains. Within a 2-h period, the number

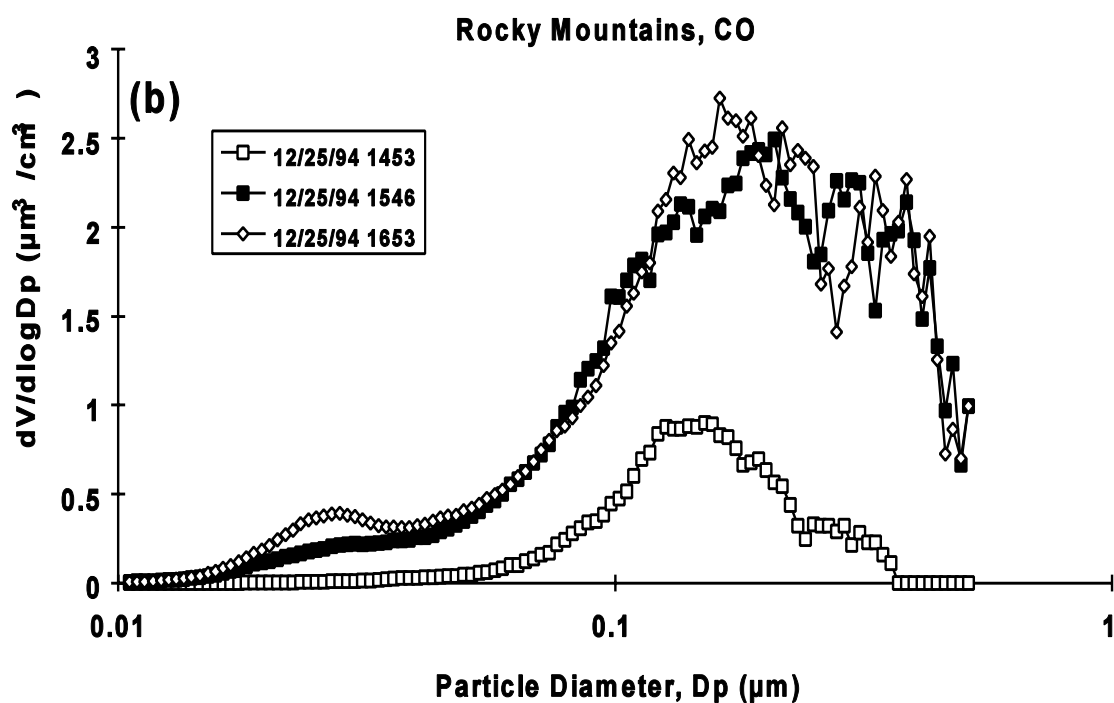
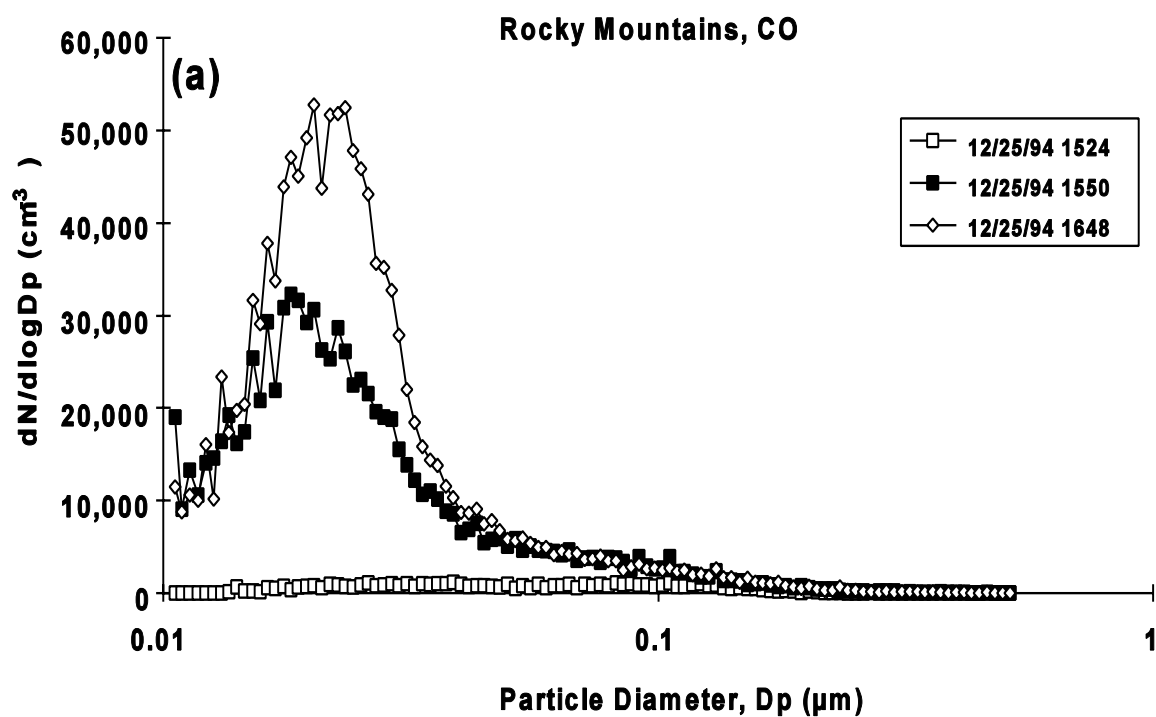


Figure 6-92. Number (a) and volume (b) size distributions at the Rocky Mountain site showing an intrusion of urban air.

concentration increased from 850 cm^{-3} to $19,000 \text{ cm}^{-3}$, an increase of more than a factor of 20. In contrast, the volume distribution increased by less than a factor of 5. The number geometric mean diameter decreased from $0.052 \text{ }\mu\text{m}$ for the background aerosol to $0.024 \text{ }\mu\text{m}$ for the urban influenced aerosol. For the urban influenced size distributions, over 96% of the particle number was measured in particles below $0.1 \text{ }\mu\text{m}$, while 80% of the particle volume was associated with particles above that size.

6.8.3 Relation of Particle Number to Particle Mass

In general, the majority of airborne particle volume and mass is associated with particles above $0.1 \text{ }\mu\text{m}$, while the highest number concentration of particles is found in particles below $0.1 \text{ }\mu\text{m}$. This was shown for volume in Figures 6-89 to 6-92 and can be seen for mass in the recent data collected in the Los Angeles, CA shown in Figure 6-93. As with the data of Whitby and Sverdrup (1980), the size distributions of Figure 6-93 show data collected by several instruments. Physical size distributions were measured with an electrical aerosol analyzer for particles between 0.01 and $0.4 \text{ }\mu\text{m}$, and with a laser optical particle counter for particles between 0.14 and $3 \text{ }\mu\text{m}$. Additionally, Berner (John et al., 1989, 1990) and MOUDI (Marple et al., 1991) impactors were used to measure the mass size distribution of inorganic ion species and carbonaceous species. These data have been combined (Hering et al., 1996) to give a total mass distribution from which the number distribution has been calculated assuming an effective aerosol density of 1.6 g/cm^3 and assuming that the water associated with the aerosol is 15% of the measured dry particle mass (see McMurry and Stolzenburg, 1989). The optical particle counter was calibrated with ambient particles, size classified by a differential mobility analyzer. The ambient aerosol has a lower effective refractive index than the polystyrene latex usually used for calibration (Hering and McMurry, 1991). No fitting was applied to match the different size distributions in the region of overlap.

Figure 6-93 shows the average of distributions collected over six different days in the fall of 1987 in downtown Los Angeles, as part of the Southern California Air Quality Study. Particle number distributions emphasize the ultrafine particles, or "nuclei" mode. Volume distributions place importance on 0.1 to $1 \text{ }\mu\text{m}$ particles which are associated with the "accumulation" mode. For this average distribution 88% of the particle number is associated with particles below 0.1

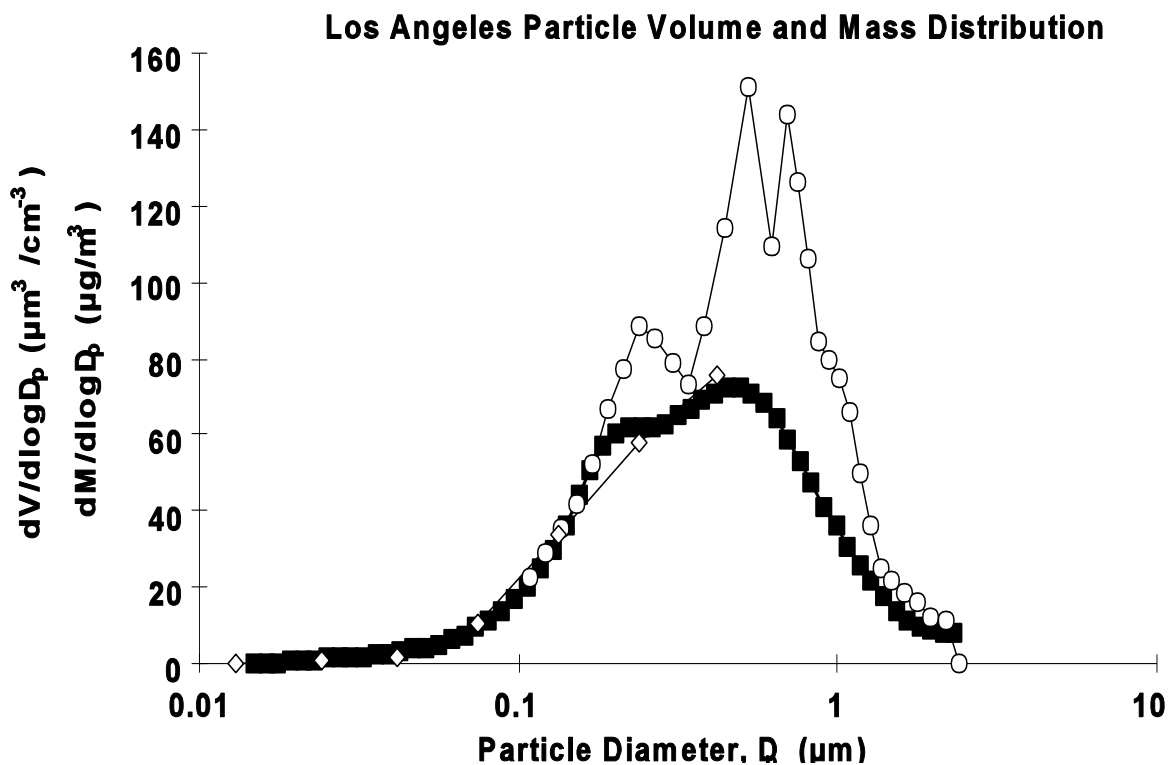
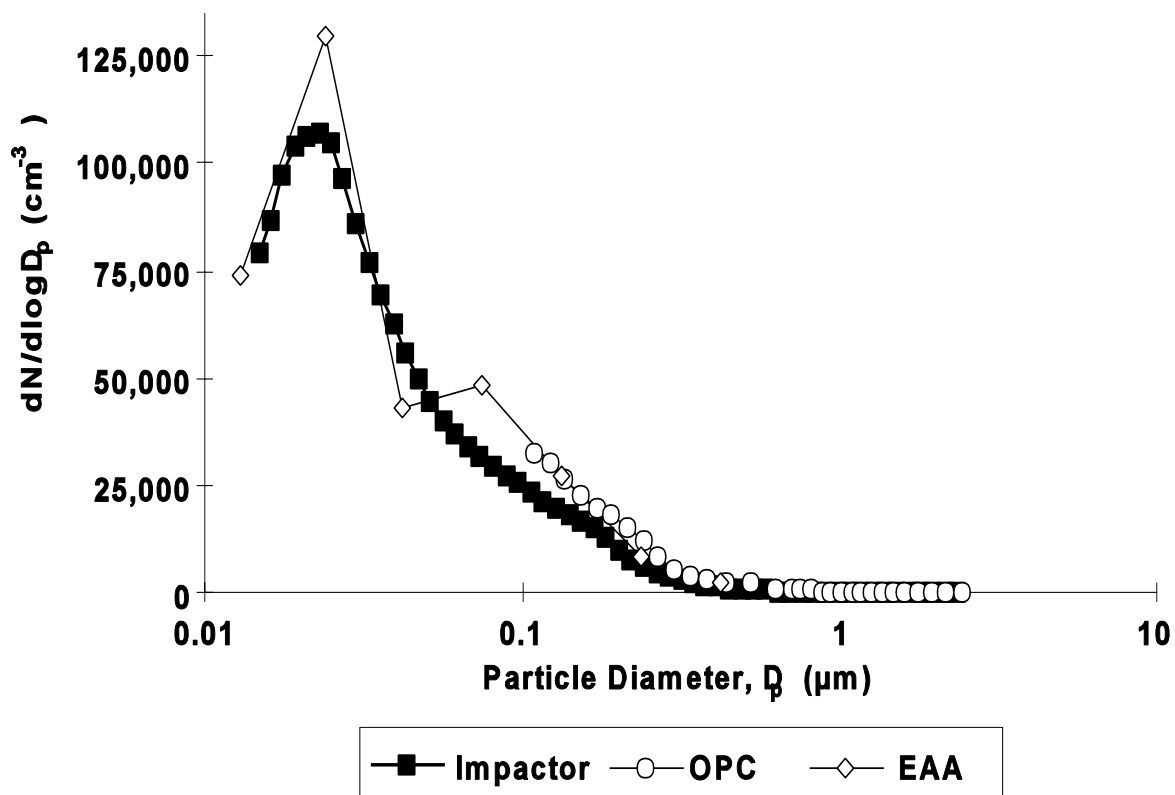


Figure 6-93. Number (a), and volume and mass (b) size distributions from Los Angeles, CA, showing comparison of three measurement techniques.

μm , but 99% of the particle volume is from particles above that size. Both the impactor and optical counter data indicate a weakly bimodal character for the accumulation mode aerosol.

For unimodal, log normal size distributions, the particle volume V is simply related to the particle number N by the relation:

$$V = \frac{\pi}{6} D_{gn}^3 \exp\left(\frac{9}{2} \ln^2 \sigma_g\right) N$$

where D_{gn} is the number geometric mean diameter, and σ_g is the geometric standard deviation. However, because of the multimodal character of ambient aerosol size distributions, one does not expect this simple relationship to hold in the atmosphere. The relationship between particle number and particle volume was examined for data from the Southern California Air Quality Study collected at Riverside, CA over 11 days in the summer of 1987, and at downtown Los Angeles in the fall of 1987 using the methods described above. As shown in Figure 6-94, particle number concentrations are correlated with the volume associated with particles below $0.1 \mu\text{m}$, but are not correlated with the total fine particle volume. Similar results are found for the data reported from Rocky Mountains, CO and for the data reported by Whitby and Sverdrup (1980).

6.8.4 Conclusion

The size distribution measurements of aerosols in urban and continental background regions indicate number geometric mean diameters which vary from 0.01 to 0.08, with the larger values found in background regions. Particle number concentrations may vary from less than $1,000/\text{cm}^3$ at clean, background sites to over $100,000/\text{cm}^3$ in polluted urban areas. Particle number concentrations are dominated by the ultrafine or nuclei mode aerosols. In contrast, the volume (or mass) of fine particles is associated with particles above $0.1 \mu\text{m}$, which are associated with the accumulation mode identified by Whitby and coworkers (Willeke and Whitby, 1975; Whitby and Sverdrup, 1980). Particle number concentrations are correlated with the volume of particles below $0.1 \mu\text{m}$. The number concentration of ultrafine particles results from a balance between formation and removal. The rate of removal by coagulation with accumulation mode

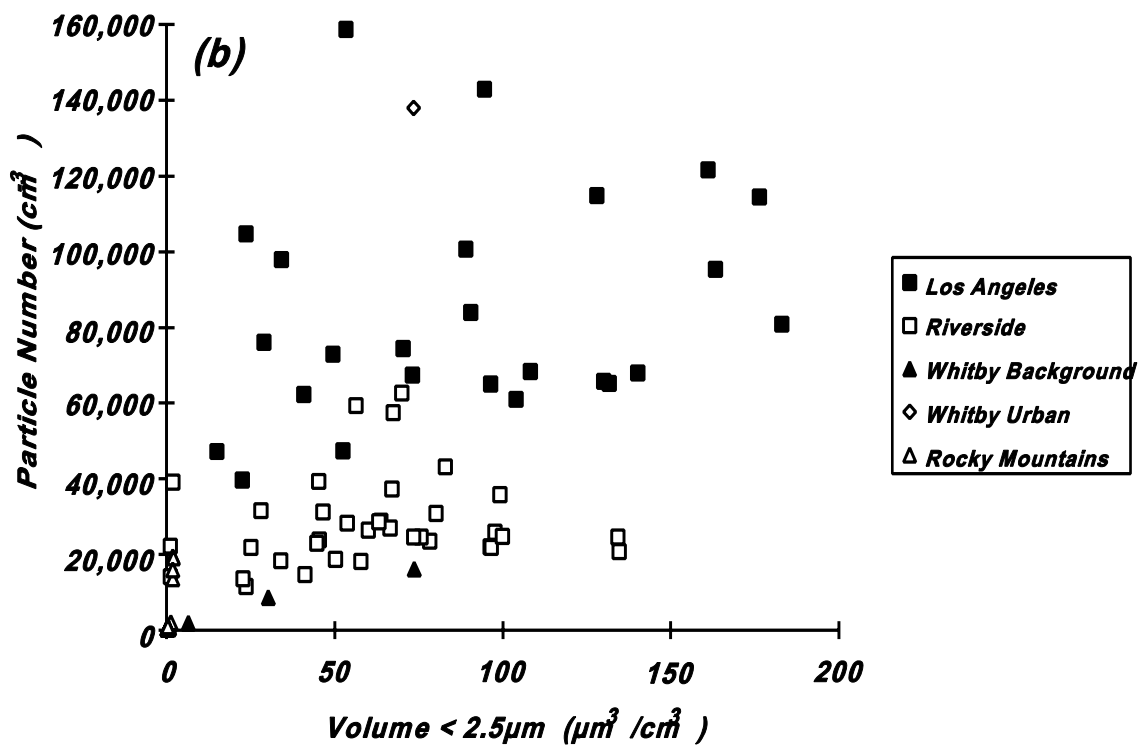
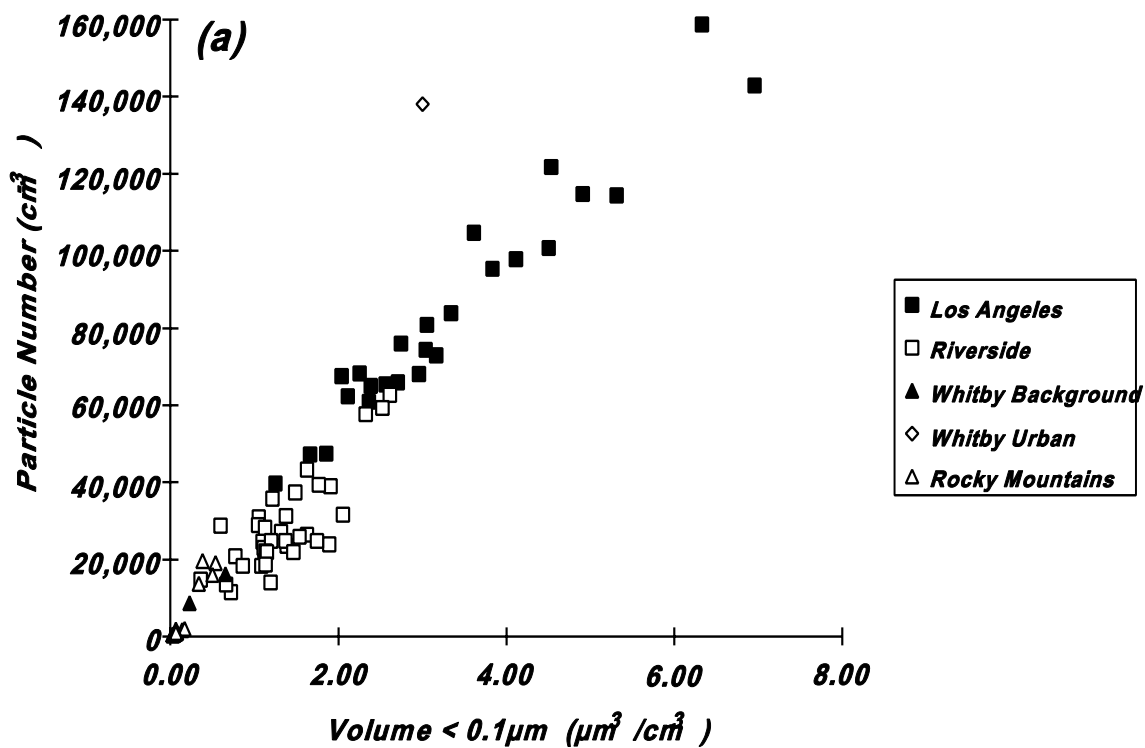


Figure 6-94. Relationship between particle number and particle volume ([a] volume < 0.1 and [b] $< 2.5 \mu\text{m}$).

particles will increase as the number (and mass and volume) of accumulation mode particles increases. Therefore, a correlation between number and accumulation mode volume or mass on a short term (e.g., hourly basis), would not be anticipated. However, as suggested by the differences in particle number concentrations from 850 cm^{-3} at a remote site in the Rocky Mountains, to $19,000 \text{ cm}^{-3}$ in air transported from an urban area, to in excess of 10^5 cm^{-3} in polluted urban areas, a correlation, between the total number concentration and the total fine article mass or volume, might be expected if comparisons were made over longer periods, e.g. days. However, no such studies have been done.

6.9 AMBIENT CONCENTRATIONS OF ULTRAFINE METALS

6.9.1 Introduction

Nucleation theory (Seinfeld, 1986) indicates that ultrafine particles will consist of materials that have very low vapor pressure but which will, at some time, exist in significant vapor concentrations. This could be the result of rapid formation of a condensible vapor from chemical conversion of a gas or the formation of a vapor at relatively high concentrations during combustion. Very small particles, because of their high curvature, have a higher vapor pressure than larger particles. This is known as the Kelvin effect and becomes increasingly important as the particle size decreases below $0.1 \mu\text{m}$ in diameter. The critical size, at which a particle will grow instead of evaporating, depends on the saturation ratio, the ratio of the vapor pressure of the particle, p_A , to the vapor pressure over a flat surface, p_A° ($S = p_A/p_A^\circ$); the surface tension; and the molar volume of the condensed phase. Thus, materials such as elemental carbon, formed in flames, or metal (or metal compound) vapor, formed during combustion, are likely candidates for ultrafine particles. Sulfuric acid can also form ultrafine particles (Weber et al., 1995) but whether it nucleates into ultrafine particles or condenses on existing particles depends on the balance between the formation rate of sulfuric acid and the surface area of preexisting particles (Seinfeld, 1986).

Thus, ultrafine aerosols may be primary, formed from vapor generated during combustion, or secondary, formed from vapor generated by chemical reactions in the atmosphere. Because of their small size, ultrafine particles diffuse rapidly and are lost by deposition to surfaces or by